

Measurement of peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN) and  
peroxymethacryloyl nitrate (MPAN) during TRACE-P.

Final Report  
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**Field Work:**

In Fall 2000, the PANs gas chromatograph (GC) was improved and prepared for installation on the NASA P-3. A number of experiments were conducted in conjunction with the NCAR NO<sub>x,y</sub> instrument (B. Ridley) to settle some of the fine details of the output of the calibration system for each instrument. In addition, the sampling frequency was improved.

We participated in the NASA TRACE-P field mission (Feb.-April, 2001) by flying the PANs GC to make measurements of PAN, PPN, PiBN, and MPAN (not detected) on 20 flights of the P-3 aircraft. The study focussed on the influence of outflow of Asian emissions on the tropospheric chemistry over the central and western Pacific Ocean. Flights originated from Wallops, went through Dryden, Hawaii, Wake Island, Guam, and Midway. Major bases were Hong Kong, China, and Yokota Air Base, Japan.

**Data Reduction and Preliminary Results:**

Pollution plumes were sampled over the western Pacific, and particularly intense pollution was sampled over the Yellow Sea, the South China Sea, the Sea of Japan, and the Pacific Ocean off the East Coast of Japan. PAN, PPN, and PiBN mixing ratios point to anthropogenic pollution being the main contributor. We collaborated with Dr. Yutaka Kondo (Nagoya University, Japan) and his group during the missions to compare calibration standards. Preliminary analysis of the flight data reveals that PAN showed an increase with altitude in the Central Pacific more distant from source regions but showed a strong increase with decreasing altitude in the Western Pacific due to pollution outflow at lower altitudes. At 6-8 km PAN mixing ratios were comparable in the two regions. Analyses to estimate the source of NO<sub>x</sub> to the more remote Pacific from PAN decomposition and to determine ozone/PAN relationships in pollution plumes were planned.

In the remainder of 2000, the data collected during the TRACE-P mission were reduced and finalized, with submission to the archive as a final data set in December of 2001. Preliminary results were presented at the first TRACE-P data workshop in November 2001. Additional results were presented at the second TRACE-P workshop in June 2002.

**TRACE-P PAN Results:**

PAN, PPN, PiBN and MPAN were measured on board the NASA P-3B aircraft during the TRACE-P mission (February to April, 2001) with 20 flights spanning a

longitude range of 100 to 300 °E and a latitude range of 10 to 40° N. Local flights were based out of Hong Kong (4) and Yokota Air Base, Japan (5) as well as one night flight out of Midway Islands. PAN mixing ratios ranged from below the limit of detection in the Pacific marine boundary layer to almost 3 ppbv, observed near Tokyo and in the Shanghai urban plume. Strongly elevated mixing ratios of PANs were also observed over the Sea of Japan, the Yellow Sea and the East and South China Seas, associated with continental outflow from Asia. Elevated PAN was also observed far removed from the continent over the central and Eastern Pacific Ocean, when pollution plumes originating from Asia were encountered. The observed ratios of different PAN species were generally consistent with anthropogenic pollution rather than biogenic sources.

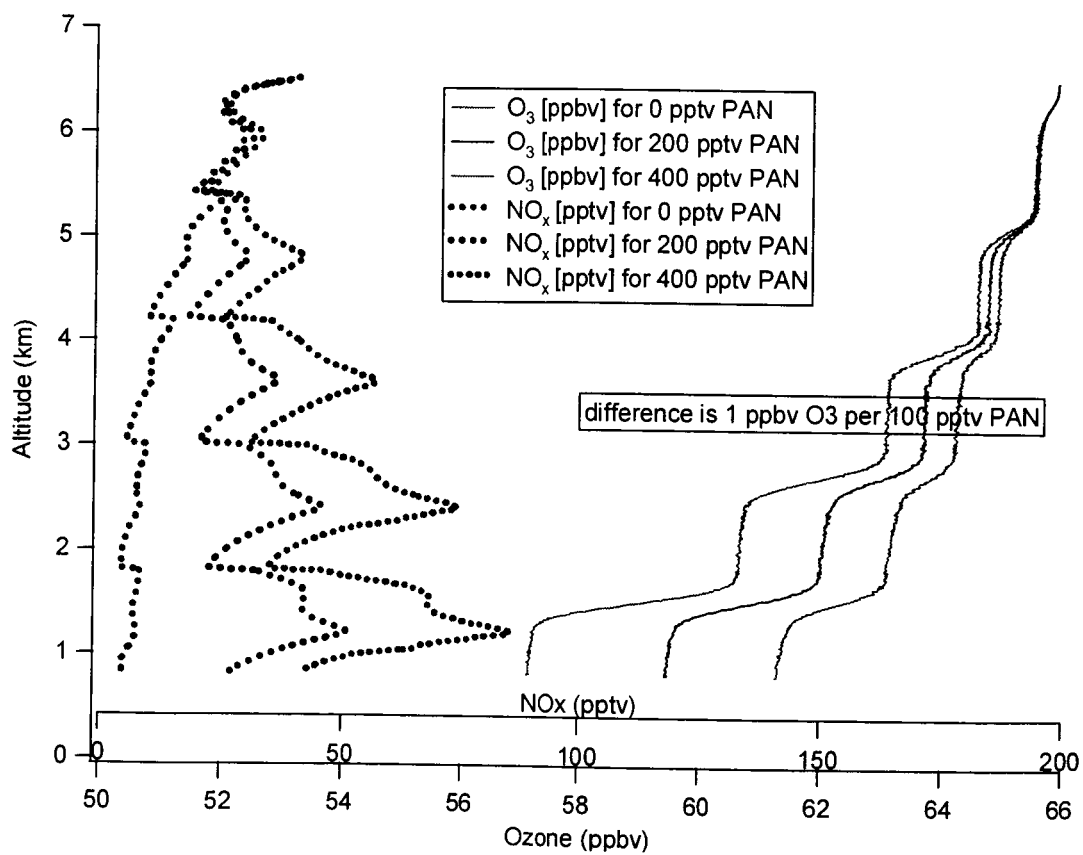
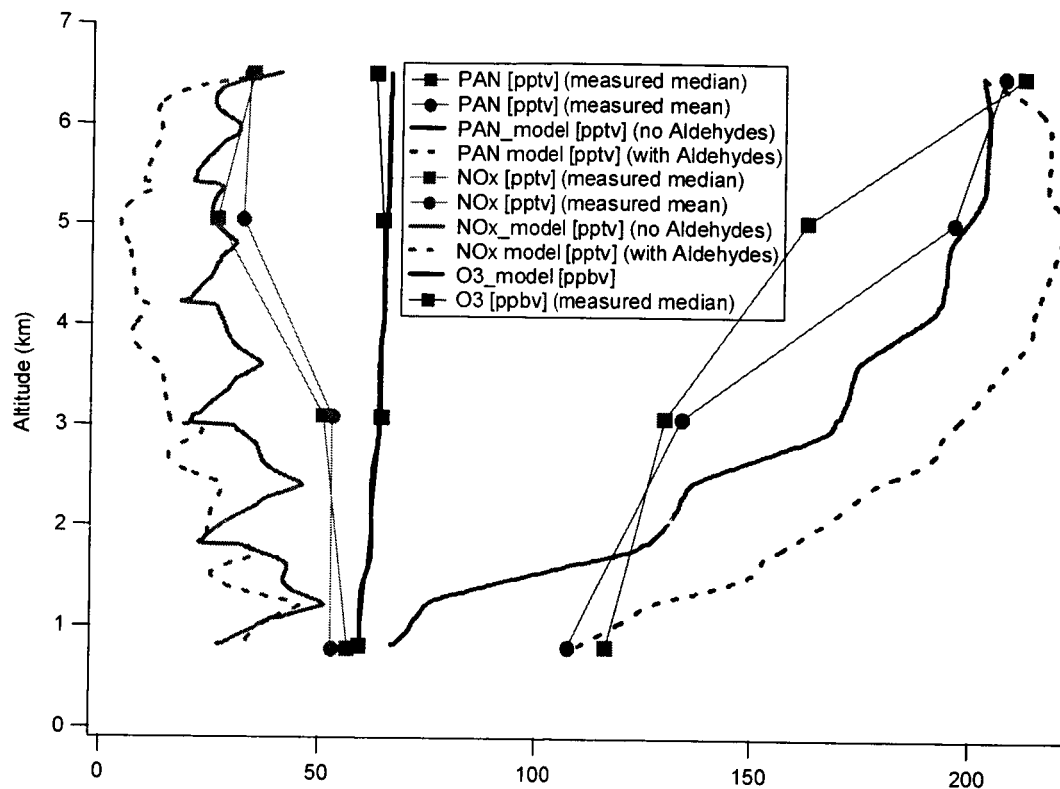
The export of PANs from polluted regions is generally viewed as a means of transporting NO<sub>x</sub> to remote regions where it may impact the chemistry of ozone upon subsidence of an air mass. Indeed profiles of PAN and NO<sub>x</sub> observed over the central Pacific by the P3 in TRACE-P suggest that the descent of air parcels and the attendant warming may foster the conversion of PAN to NO<sub>x</sub>. The median vertical profiles of PAN and NO<sub>x</sub> for three latitude bins (Asia/Western Pacific, Central Pacific and Eastern Pacific) were simulated in box models runs with imposed density and temperature time series to simulate descent. Also simulated was the impact of the NO<sub>x</sub> liberated from PAN decomposition on the profile of O<sub>3</sub>.

Figure 1 (upper panel) shows a comparison of the measured profiles of PAN, NO<sub>x</sub>, and ozone with those obtained by modeling the descent of an air parcel from 6 km that is initialized with median measured values and which descends at 1.2 km/day through the observed temperature profile. As the air parcel descends in the model, PAN dissociates at an increasing rate, resulting in a release of NO<sub>x</sub>, which becomes available to affect ozone chemistry. The ozone profile, however, shows little variation, in both the model and the observations. The lower panel illustrates the effect of the initial mixing ratio of PAN on ozone. The sensitivity of low-level O<sub>3</sub> to initial PAN at 6 km, prior to descent of the air parcel, is about 1 ppbv O<sub>3</sub> per 100 pptv PAN. The median value at 6 km for 160-200°E is 200 pptv, so the effect of PAN is to counteract the net destruction that occurs during descent by an amount of 2 ppbv. The upper panel of figure 1 also shows two model runs with the measured aldehyde mixing ratios and with the aldehydes set to zero. The measured aldehyde mixing ratios of about 150 pptv for acetaldehyde and 75 pptv for propionaldehyde do not agree with the observations of PANs and NO<sub>x</sub> over the remote Pacific Ocean. Such high aldehyde mixing ratios would remove all NO<sub>x</sub> in a period of less than a day and convert it back to PAN. Similar circumstances were observed in the arctic boundary layer during TOPSE. Ambient measurements of aldehydes in remote areas must be reevaluated with respect to inlet artifacts or other interferences.

This work, which is the subject of a publication in preparation, was presented at AGU meeting Fall 2002:

Flocke, F., A. Weinheimer, Y. Kondo, M. Koike; F. Eisele, M. Zondlo, D. Blake, S. Vay, M. Avery, G. Sachse, H. Singh, D. Westberg, H. Fuelberg, J. Crawford, Observations of PANs on Board the NASA P-3 During TRACE-P, *Eos. Trans. AGU*, 83(47), Fall Meet. Suppl., Abstract A62A-0133, 2002.

Figure 1:



### **TRACE-P Publications:**

We contributed to the following TRACE-P publications:

Cantrell, C.A., G.D. Edwards, S. Stephens, R.L. Mauldin, M. Zondlo, E. Kosciuch, F.L. Eisele, R.E. Shetter, B.L. Lefer, S. Hall, F. Flocke, A. Weinheimer, A. Fried, E. Apel, Y. Kondo, D.R. Blake, N. Blake, I. Simpson, A. Bandy, D. Thornton, B. Heikes, H. Singh, W. Brune, H. Harder, M. Martinez-Harder, M.A. Avery, S. Vay, J.D. Barrick, G.W. Sachse, J.R. Olsen, J.H. Crawford, Peroxy Radical Behavior during TRACE-P as Measured Aboard the NASA P-3B Aircraft, *J. Geophys. Res.*, 108(D20), 8797, doi:10.1029/2002JD003674, 2003.

Koike, M., Y. Kondo, K. Kita, N. Takegawa, Y. Masui, Y. Miyazaki, M.W. Ko, R.J. Weber, D.C. Thornton, G.W. Sachse, S.A. Vay, D.R. Blake, D.G. Streets, F. Flocke, A.J. Weinheimer, F.L. Eisele, S.T. Sandholm, H.B. Singh, and R.W. Talbot, Export of anthropogenic reactive nitrogen and sulfur compounds from the East Asia region in spring, *J. Geophys. Res.*, 108(D20), 8789, doi:10.1029/2002JD003284, 2003.

Eisele, F.L., L. Mauldin, C. Cantrell, M. Zondlo, E. Apel, A. Fried, R. Shetter, F. Flocke, A. Weinheimer, M. Avery, S. Vay, G. Sachse, H. Singh, W. Brune, A. Bandy, B. Heikes, Y. Kondo, D. Riemer, S. Sandholm, D. Tan, R. Talbot, and J. Dibb, Summary of measurement intercomparisons during TRACE-P, *J. Geophys. Res.*, 108(D20), 8791, doi:10.1029/2002JD003167, 2003.

Miyazaki, Y., Y. Kondo, M. Koike, H.E. Fuelberg, C.M. Kiley, K. Kita, N. Takegawa, G.W. Sachse, F. Flocke, A.J. Weinheimer, H.B. Singh, F.L. Eisele, M. Zondlo, R.W. Talbot, S.T. Sandholm, M.A. Avery, and D.R. Blake, Synoptic-scale transport of reactive nitrogen over the western Pacific in spring, *J. Geophys. Res.*, 108(D20), 8788, doi:10.1029/2002JD003248, 2003.

Kondo, Y., Y. Morino, N. Takegawa, M. Koike, K. Kita, Y. Miyazaki, G.W. Sachse, S. A. Vay, M.A. Avery, F. Flocke, A.J. Weinheimer, F. L. Eisele, M. Zondlo, R.J. Weber, H.B. Singh, G. Chen, J. Crawford, D.R. Blake, H.E. Fuelberg, A.D. Clarke, R.W. Talbot, S.T. Sandholm, E.V. Browell, D.G. Streets, and B. Liley, Impacts of Biomass Burning in Southeast Asia on Ozone and Reactive Nitrogen over the Western Pacific in Spring *J. Geophys. Res.*, submitted.

### **PAN GC Characterization (Post-TRACE-P):**

The dual-channel, fast gas chromatograph (fast PAN-GC) with electron capture detection (that flew in TRACE-P) was cross-calibrated against a total nitrogen oxide (NO<sub>y</sub>) instrument for the measurement of the peroxyacyl nitrates (PANs). The intercalibration determined the sensitivity of the fast PAN-GC for C<sub>2</sub>-C<sub>4</sub> PANs by using a secondary preparative GC to purify synthesized liquid diffusion standards, which were subsequently analyzed on the fast PAN-GC and the NO<sub>y</sub> instrument. Results demonstrated a 95.5 ± 0.5 % conversion efficiency for PAN from the photolytic calibration source, and defined the response factors relative to that of PAN as 0.90, 0.64, and 0.55 for PPN, MPAN, and PiBN, respectively. This work was carried out in

collaboration with Jim Roberts at NOAA AL. Results will be presented along with a full analytical description of the fast PAN-GC system in an article that is in preparation for submission to the Journal of Analytical Chemistry.

#### **PAN TD-CIMS Development and Characterization (for Future Missions):**

The current work of the PAN group, in collaboration with GIT (G. Huey, D. Tanner) focuses on the development and characterization of a novel Thermal Dissociation - Chemical Ionization Mass Spectrometer (TD-CIMS) method to replace the fast PAN-GC for the atmospheric measurement of peroxyacetyl nitrate compounds. The TD-CIMS system was newly developed by a collaborative group of scientists at NCAR and the Georgia Institute of Technology (Slusher et al., 2003). The ionization scheme uses a 10 mCi  $\text{Po}^{210}$  source to ionize  $\text{CH}_3\text{I}$  to  $\text{I}^-$  by alpha particle bombardment. The  $\text{I}^-$  reacts with acyl peroxy radicals generated by the thermal dissociation of the PAN compounds in front of the inlet to form the acyl ion which is detected in the mass analyzer. The very low ionization potential of  $\text{I}^-$  leads to a very selective ionization process that only reacts with the acyl peroxy radical species, and a few nitrogen oxide species ( $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ ). This method currently demonstrates a 3-10 pptv detection limit with a 1-10 second time resolution for PAN, PPN, PiBN, and APAN. Therefore the method will be ideally suited for fast measurements of fluxes in the boundary layer or for emission plumes on aircraft platforms. Atmospheric concentrations of PAN, and PPN, as measured by the TD-CIMS instrument showed good agreement ( $\pm 10\%$ ) with those of our fast PAN-GC under field conditions. See Figure 2.

A detailed laboratory characterization of the TD-CIMS instrument has been carried out in preparation for deployment on the NOAA P-3 research aircraft for the NENA campaign in summer 2004. The TD-CIMS has been cross-calibrated against the fast PAN-GC and against the  $\text{NO}_y$  instrument to determine calibration factors and relative sensitivities for the PAN homologues (PAN, PPN, PiBN, and MPAN) on the TD-CIMS. In addition, the PAN homologues have been produced in a 50 liter reaction chamber at the NCAR/ACD kinetics lab, in collaboration with Geoff Tyndall and John Orlando, where the TD-CIMS was cross calibrated against the long path FTIR connected to the reaction chamber. Additionally, some novel PAN homologues (1-hydroxyl-peroxyacetyl nitrate (HPAN), methoxyformyl nitrate (MoPN, and peroxybenzoyl nitrate (PBzN)) were also produced in the chamber to investigate the TD-CIMS measurement capabilities. HPAN appears to be very short lived under ambient conditions and the sensitivity could not be determined, while MoPN and PBzN had equivalent sensitivities to PAN on the TD-CIMS.

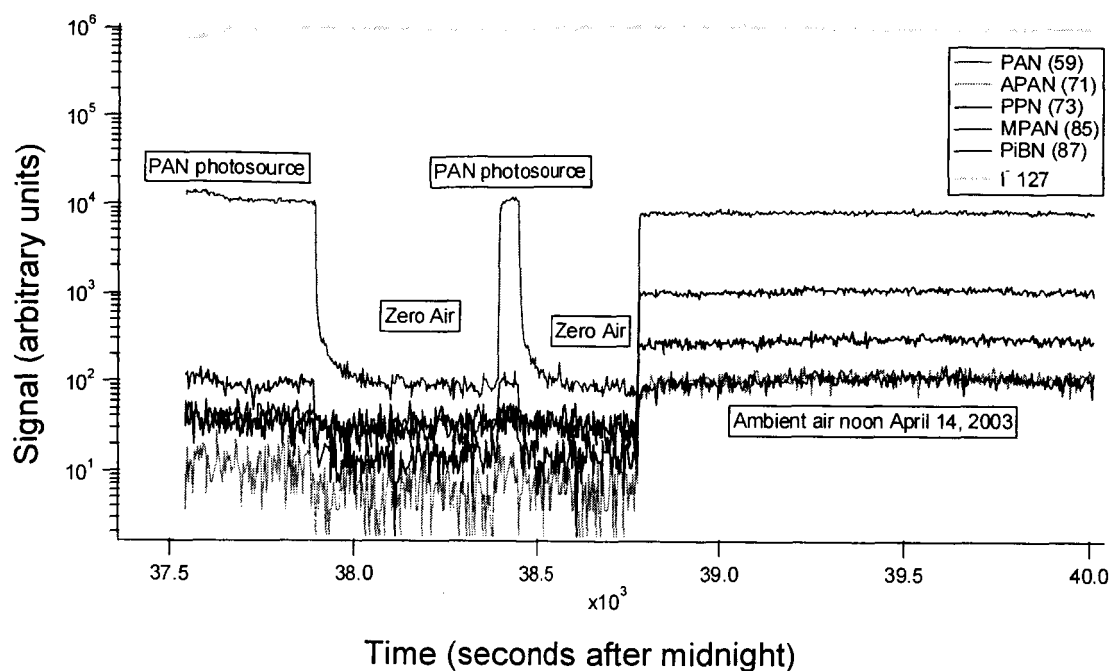


Figure 2. Time series of PANs measurements using the new TD-CIMS showing low background counts (left half) while sampling zero air and sensitive response (right half) when sampling outside air. A calibration signal from the PAN photosource is intermittently superimposed while on zero air. Note the logarithmic scale on the vertical axis.